

# **EXHIBIT 111**

**ASBESTOS by TEM****7402**

FORMULA: Various

MW: Various

CAS: Various

RTECS: Various

METHOD: 7402

EVALUATION: PARTIAL

Issue 1: 15 May 1989

Issue 2: 15 August 1994

**OSHA :** 0.1 asbestos fibers (>5 µm long)/cc;  
1 f/cc/30 min excursion; carcinogen

**MSHA:** 2 asbestos fibers/cc

**NIOSH:** 0.1 f/cc (fibers > 5 µm long)/400 L; carcinogen

**ACGIH:** 0.2 crocidolite; 0.5 amosite; 2 chrysotile  
and other asbestos, fibers/cc; carcinogen

**PROPERTIES:** solid, fibrous, crystalline,  
anisotropic

**SYNONYMS [CAS#]:** actinolite [77536-66-4] or ferroactinolite [15669-07-5]; amosite [12172-73-5]; anthophyllite [77536-67-5]; chrysotile [12001-29-5]; serpentine [18786-24-8]; crocidolite [12001-28-4]; tremolite [77536-68-6]; amphibole asbestos [1332-21-4].

SAMPLING		MEASUREMENT	
<b>SAMPLER:</b>	FILTER (0.45- to 1.2-µm cellulose ester membrane, 25-mm diameter; conductive cassette)	<b>TECHNIQUE:</b>	MICROSCOPY, TRANSMISSION ELECTRON (TEM)
<b>FLOW RATE:</b>	0.5 to 16 L/min	<b>ANALYTE:</b>	asbestos fibers
<b>VOL-MIN*:</b>	400 L @ 0.1 fiber/cc	<b>SAMPLE PREPARATION:</b>	modified Jaffe wick
<b>-MAX*:</b>	(step 4, sampling) *Adjust for 100 to 1300 fibers/mm <sup>2</sup>	<b>EQUIPMENT:</b>	transmission electron microscope; energy dispersive X-ray system (EDX) analyzer
<b>SHIPMENT:</b>	routine (pack to reduce shock)	<b>CALIBRATION:</b>	qualitative electron diffraction; calibration of TEM magnification and EDX system
<b>SAMPLE STABILITY:</b>	stable	<b>RANGE:</b>	100 to 1300 fibers/mm <sup>2</sup> filter area [1]
<b>BLANKS:</b>	2 to 10 field blanks per set	<b>ESTIMATED LOD:</b>	1 confirmed asbestos fiber above 95% of expected mean blank value
ACCURACY		<b>PRECISION (<math>\bar{S}_p</math>):</b>	0.28 when 65% of fibers are asbestos; 0.20 when adjusted fiber count is applied to PCM count [2].
<b>RANGE STUDIED:</b>	80 to 100 fibers counted		
<b>BIAS:</b>	not determined		
<b>OVERALL PRECISION (<math>\bar{S}_{pr}</math>):</b>	see EVALUATION OF METHOD		
<b>ACCURACY:</b>	not determined		

**APPLICABILITY:** The quantitative working range is 0.04 to 0.5 fiber/cc for a 1000-L air sample. The LOD depends on sample volume and quantity of interfering dust, and is <0.01 fiber/cc for atmospheres free of interferences. This method is used to determine asbestos fibers in the optically visible range and is intended to complement the results obtained by phase contrast microscopy (Method 7400).

**INTERFERENCES:** Other amphibole particles that have aspect ratios greater than 3:1 and elemental compositions similar to the asbestos minerals may interfere in the TEM analysis. Some non-amphibole minerals may give electron diffraction patterns similar to amphiboles. High concentrations of background dust interfere with fiber identification. Some non-asbestos amphibole minerals may give electron diffraction patterns similar to asbestos amphiboles.

**OTHER METHODS:** This method is designed for use with Method 7400 (phase contrast microscopy).

**REAGENTS:**

1. Acetone. (See SPECIAL PRECAUTIONS.)

**EQUIPMENT:**

1. Sampler: field monitor, 25-mm, three-piece cassette with ca. 50-mm electrically-conductive extension cowl, cellulose ester membrane filter, 0.45- to 1.2- $\mu$ m pore size, and backup pad.  
NOTE 1: Analyze representative filters for fiber background before use. Discard the filter lot if mean count is  $>5$  fibers/100 fields. These are defined as laboratory blanks.  
NOTE 2: Use an electrically-conductive extension cowl to reduce electrostatic effects on fiber sampling and during sample shipment. Ground the cowl when possible during sampling.  
NOTE 3: 0.8- $\mu$ m pore size filters are recommended for personal sampling. 0.45- $\mu$ m filters are recommended for sampling when performing TEM analysis on the samples because the particles deposit closer to the filter surface. However, the higher pressure drop through these filters normally preclude their use with personal sampling pumps.
2. Personal sampling pump, 0.5 to 16 L/min, with flexible connecting tubing.
3. Microscope, transmission electron, operated at ca. 100 kV, with electron diffraction and energy-dispersive X-ray capabilities, and having a fluorescent screen with inscribed or overlaid calibrated scale (Step 15).  
NOTE: The scale is most efficient if it consists of a series of lines inscribed on the screen or partial circles every 2 cm distant from the center.
4. Diffraction grating replica with known number of lines/mm.
5. Slides, glass, pre-cleaned, 25- x 75-mm.
6. Knife, surgical steel, curved-blade.
7. Tweezers.
8. Grids, 200-mesh TEM copper, (optional: carbon-coated).
9. Petri dishes, 15-mm depth. The top and bottom of the petri dish must fit snugly together. To assure a tight fit, grind the top and bottom pieces together with an abrasive such as carborundum to produce a ground-glass contact surface.
10. Foam, clean polyurethane, spongy, 12-mm thick.
11. Filters, Whatman No. 1 qualitative paper or equivalent, or lens paper.
12. Vacuum evaporator.
13. Cork borer, (about 8-mm).
14. Pen, waterproof, marking.
15. Reinforcement, page, gummed.
16. Asbestos standard bulk materials for reference; e.g. SRM #1866, available from the National Institute of Standards and Technology.
17. Carbon rods, sharpened to 1 mm x 8 mm.
18. Microscope, light, phase contrast (PCM), with Walton-Beckett graticule (see method 7400).
19. Grounding wire, 22-gauge, multi-strand.
20. Tape, shrink- or adhesive-.

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**SPECIAL PRECAUTIONS:** Acetone is extremely flammable (flash point = 0 °F). Take precautions not to ignite it. Heating of acetone must be done in a fume hood using a flameless, spark-free heat source. Asbestos is a confirmed human carcinogen. Handle only in a well-ventilated fume hood.

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**SAMPLING:**

1. Calibrate each personal sampling pump with a representative sampler in line.
2. For personal sampling, fasten sampler to worker's lapel near worker's mouth. Remove the top cover from cowl extension ("open-face") and orient sampler face down. Wrap joint between extender and monitor body with tape to help hold the cassette together and provide a marking surface to identify the cassette. Where possible, especially at low %RH, attach sampler to electrical ground to reduce electrostatic effects during sampling.
3. Submit at least two field blanks (or 10% of the total samples, whichever is greater) for each set of samples. Remove top covers from the field blank cassettes and store top covers and cassettes in a clean area (e.g., closed bag or box) during sampling. Replace top covers when sampling is completed.
4. Sample at 0.5 to 16 L/min [3]. Adjust sampling rate,  $Q$  (L/min), and time,  $t$  (min), to produce fiber density,  $E$ , of 100 to 1300 fibers/mm<sup>2</sup> [ $3.85 \cdot 10^4$  to  $5 \cdot 10^5$  fibers per 25-mm filter with effective collection area ( $A_c = 385 \text{ mm}^2$ )] for optimum accuracy. Do not exceed ca. 0.5 mg total dust loading on the filter. These variables are related to the action level (one-half the current standard),  $L$  (fibers/cc), of the fibrous aerosol being sampled by:

$$t = \frac{A_c \cdot E}{Q \cdot L \cdot 10^3}, \text{ min.}$$

NOTE: The purpose of adjusting sampling times is to obtain optimum fiber loading on the filter. A sampling rate of 1 to 4 L/min for 8 h (700 to 2800 L) is appropriate in atmospheres containing ca. 0.1 fiber/cc in the absence of significant amounts of non-asbestos dust. Dusty atmospheres require smaller sample volumes ( $\leq 400$  L) to obtain countable samples. In such cases take short, consecutive samples and average the results over the total collection time. For documenting episodic exposures, use high rates (7 to 16 L/min) over shorter sampling times. In relatively clean atmospheres, where targeted fiber concentrations are much less than 0.1 fiber/cc, use larger sample volumes (3000 to 10000 L) to achieve quantifiable loadings. Take care, however, not to overload the filter with background dust [3].

5. At the end of sampling, replace top cover and small end caps.
6. Ship samples upright with conductive cowl attached in a rigid container with packing material to prevent jostling or damage.

NOTE: Do not use untreated polystyrene foam in the shipping container because electrostatic forces may cause fiber loss from sample filter.

**SAMPLE PREPARATION:**

7. Remove circular sections from any of three quadrants of each sample and blank filter using a cork borer [4]. The use of three grid preparations reduces the effect of local variations in dust deposit on the filter.
8. Affix the circular filter sections to a clean glass slide with a gummed page reinforcement. Label the slide with a waterproof marking pen.  
NOTE: Up to eight filter sections may be attached to the same slide.
9. Place the slide in a petri dish which contains several paper filters soaked with 2 to 3 mL acetone. Cover the dish. Wait 2 to 4 min for the sample filter(s) to fuse and clear.  
NOTE: The "hot block" clearing technique [5] of Method 7400 or the DMF clearing technique [6] may be used instead of steps 8 and 9.
10. Transfer the slide to a rotating stage inside the bell jar of a vacuum evaporator. Evaporate a 1-by 5-mm section of a graphite rod onto the cleared filter(s). Remove the slide to a clean, dry, covered petri dish [4].
11. Prepare a second petri dish as a Jaffe wick washer with the wicking substrate prepared from filter or lens paper placed on top of a 12-mm thick disk of clean, spongy polyurethane foam [7].

Cut a V-notch on the edge of the foam and filter paper. Use the V-notch as a reservoir for adding solvent.

NOTE: The wicking substrate should be thin enough to fit into the petri dish without touching the lid.

12. Place the TEM grid on the filter or lens paper. Label the grids by marking with a pencil on the filter paper or by putting registration marks on the petri dish halves and marking with a waterproof marker on the dish lid. In a fume hood, fill the dish with acetone until the wicking substrate is saturated.  
NOTE: The level of acetone should be just high enough to saturate the filter paper without creating puddles.
13. Remove about a quarter section of the carbon-coated filter from the glass slide using a surgical knife and tweezers. Carefully place the excised filter, carbon side down, on the appropriately-labeled grid in the acetone-saturated petri dish. When all filter sections have been transferred, slowly add more solvent to the wedge-shaped trough to raise the acetone level as high as possible without disturbing the sample preparations. Cover the petri dish. Elevate one side of the petri dish by placing a slide under it (allowing drops of condensed acetone to form near the edge rather than in the center where they would drip onto the grid preparation).

#### CALIBRATION AND QUALITY CONTROL:

14. Determine the TEM magnification on the fluorescent screen:
  - a. Define a field of view on the fluorescent screen either by markings or physical boundaries.  
NOTE: The field of view must be measurable or previously inscribed with a scale or concentric circles (all scales should be metric) [7].
  - b. Insert a diffraction grating replica into the specimen holder and place into the microscope. Orient the replica so that the grating lines fall perpendicular to the scale on the TEM fluorescent screen. Ensure that goniometer stage tilt is zero.
  - c. Adjust microscope magnification to 10,000X. Measure the distance (mm) between the same relative positions (e.g., between left edges) of two widely-separated lines on the grating replica. Count the number of spaces between the lines.  
NOTE: On most microscopes the magnification is substantially constant only within the central 8- to 10-cm diameter region of the fluorescent screen.
  - d. Calculate the true magnification (M) on the fluorescent screen:

$$m = \frac{X \cdot G}{Y}$$

where: X = total distance (mm) between the two grating lines;  
G = calibration constant of the grating replica (lines/mm);  
Y = number of grating replica spaces counted

- e. After calibration, note the apparent sizes of 0.25 and 5.0  $\mu\text{m}$  on the fluorescent screen. (These dimensions are the boundary limits for counting asbestos fibers by phase contrast microscopy.)
15. Measure 20 grid openings at random on a 200-mesh copper grid by placing a grid on a glass slide and examining it under the PCM. Use the Walton-Beckett graticule to measure the grid opening dimensions. Calculate an average graticule field dimension from the data and use this number to calculate the graticule field area for an average grid opening.  
NOTE: A grid opening is considered as one graticule field.
16. Obtain reference selected area electron diffraction (SAED) or microdiffraction patterns from standard asbestos materials prepared for TEM analysis.  
NOTE: This is a visual reference technique. No quantitative SAED analysis is required [7]. Microdiffraction may produce clearer patterns on very small fibers or fibers partially obscured by other material.
  - a. Set the specimen holder at zero tilt.

- b. Center a fiber, focus, and center the smallest field-limiting aperture on the fiber. Obtain a diffraction pattern. Photograph each distinctive pattern and keep the photo for comparison to unknowns.  
NOTE: Not all fibers will present diffraction patterns. The objective lens current may need adjustment to give optimum pattern visibility. There are many more amphiboles which give diffraction patterns similar to the analytes named on p. 7402-1. Some, but not all, of these can be eliminated by chemical separations. Also, some non-amphiboles (e.g., pyroxenes, some talc fibers) may interfere.
17. Acquire energy-dispersive X-ray (EDX) spectra on approximately 5 fibers having diameters between 0.25 and 0.5  $\mu\text{m}$  of each asbestos variety obtained from standard reference materials [7].  
NOTE: The sample may require tilting to obtain adequate signal. Use same tilt angle for all spectra.
  - a. Prepare TEM grids of all asbestos varieties.
  - b. Use acquisition times (at least 100 sec) sufficient to show a silicon peak at least 75% of the monitor screen height at a vertical scale of  $\geq 500$  counts per channel.
  - c. Estimate the elemental peak heights visually as follows:
    - (1) Normalize all peaks to silicon (assigned an arbitrary value of 10).
    - (2) Visually interpret all other peaks present and assign values relative to the silicon peak.
    - (3) Determine an elemental profile for the fiber using the elements Na, Mg, Si, Ca, and Fe. Example: 0-4-10-3-<1 [7].  
NOTE: In fibers other than asbestos, determination of Al, K, Ti, S, P, and F may also be required for fiber characterization.
    - (4) Determine a typical range of profiles for each asbestos variety and record the profiles for comparison to unknowns.

**MEASUREMENT:**

18. Perform a diffraction pattern inspection on all sample fibers counted under the TEM, using the procedures given in step 17. Assign the diffraction pattern to one of the following structures:
  - a. chrysotile;
  - b. amphibole;
  - c. ambiguous;
  - d. none.  
NOTE: There are some crystalline substances which exhibit diffraction patterns similar to those of asbestos fibers. Many of these, (brucite, halloysite, etc.) can be eliminated from consideration by chemistry. There are, however, several minerals (e.g., pyroxenes, massive amphiboles, and talc fibers) which are chemically similar to asbestos and can be considered interferences. The presence of these substances may warrant the use of more powerful diffraction pattern analysis before positive identification can be made. If interferences are suspected, morphology can play an important role in making positive identification.
19. Obtain EDX spectra in either the TEM or STEM modes from fibers on field samples using the procedure of step 18. Using the diffraction pattern and EDX spectrum, classify the fiber:
  - a. For a chrysotile structure, obtain EDX spectra on the first five fibers and one out of ten thereafter. Label the range profiles from 0-5-10-0-0 to 0-10-10-0-0 as "chrysotile."
  - b. For an amphibole structure, obtain EDX spectra on the first 10 fibers and one out of ten thereafter. Label profiles ca. 0-2-10-0-7 as "possible amosite"; profiles ca. 1-1-10-0-6 as "possible crocidolite"; profiles ca. 0-4-10-3-<1 as "possible tremolite"; and profiles ca. 0-3-10-0-1 as "possible anthophyllite."  
NOTE: The range of profiles for the amphiboles will vary up to  $\pm 1$  unit for each of the elements present according to the relative detector efficiency of the spectrometer.
  - c. For an ambiguous structure, obtain EDX spectra on all fibers. Label profiles similar to the chrysotile profile as "possible chrysotile." Label profiles similar to the various amphiboles as "possible amphiboles." Label all others as "unknown" or "non-asbestos."

## 20. Counting and Sizing:

- a. Insert the sample grid into the specimen grid holder and scan the grid at zero tilt at low magnification (ca. 300 to 500X). Ensure that the carbon film is intact and unbroken over ca. 75% of the grid openings.
- b. In order to determine how the grids should be sampled, estimate the number of fibers per grid opening during a low-magnification scan (500 to 1000X). This will allow the analyst to cover most of the area of the grids during the fiber count and analysis. Use the following rules when picking grid openings to count [7,8]:
  - (1) Light loading (<5 fibers per grid opening): count total of 40 grid openings.
  - (2) Moderate loading (5 to 25 fibers per grid opening): count minimum of 40 grid openings or 100 fibers.
  - (3) Heavy loading (>25 fibers per opening): count a minimum of 100 fibers and at least 6 grid openings.

Note that these grid openings should be selected approximately equally among the three grid preparations and as randomly as possible from each grid.

- c. Count only grid openings that have the carbon film intact. At 500 to 1000X magnification, begin counting at one end of the grid and systematically traverse the grid by rows, reversing direction at row ends. Select the number of fields per traverse based on the loading indicated in the initial scan. Count at least 2 field blanks per sample set to document possible contamination of the samples. Count fibers using the following rules:
  - (1) Count all particles with diameter greater than 0.25  $\mu\text{m}$  that meet the definition of a fiber (aspect ratio  $\geq 3:1$ , longer than 5  $\mu\text{m}$ ). Use the guideline of counting all fibers that would have been counted under phase contrast light microscopy (Method 7400). Use higher magnification (10000X) to determine fiber dimensions and countability under the acceptance criteria. Analyze a minimum of 10% of the fibers, and at least 3 asbestos fibers, by EDX and SAED to confirm the presence of asbestos. Fibers of similar morphology under high magnification can be identified as asbestos without SAED. Particles which are of questionable morphology should be analyzed by SAED and EDX to aid in identification.
  - (2) Count fibers which are partially obscured by the grid as half fibers.  
NOTE: If a fiber is partially obscured by the grid bar at the edge of the field of view, count it as a half fiber only if more than 2.5  $\mu\text{m}$  of fiber is visible.
  - (3) Size each fiber as it is counted and record the diameter and length:
    - (a) Move the fiber to the center of the screen. Read the length of the fiber directly from the scale on the screen.  
NOTE 1: Data can be recorded directly off the screen in  $\mu\text{m}$  and later converted to  $\mu\text{m}$  by computer.  
NOTE 2: For fibers which extend beyond the field of view, the fiber must be moved and superimposed upon the scale until its entire length has been measured.
    - (b) When a fiber has been sized, return to the lower magnification and continue the traverse of the grid area to the next fiber.
- d. Record the following fiber counts:
  - (1)  $f_s$ ,  $f_b$  = number of asbestos fibers in the grid openings analyzed on the sample filter and corresponding field blank, respectively.
  - (2)  $F_s$ ,  $F_b$  = number of fibers, regardless of identification, in the grid openings analyzed on the sample filter and corresponding field blank, respectively.

**CALCULATIONS:**

21. Calculate and report the fraction of optically visible asbestos fibers on the filter,  $(f_s - f_b)/(F_s - F_b)$ . Apply this fraction to fiber counts obtained by PCM on the same filter or on other filters for which the TEM sample is representative. The final result is an asbestos fiber count. The type of asbestos present should also be reported.
22. As an integral part of the report, give the model and manufacturer of the TEM as well as the model and manufacturer of the EDX system.

**EVALUATION OF METHOD:**

The TEM method, using the direct count of asbestos fibers, has been shown to have a precision of 0.275 ( $s_r$ ) in an evaluation of mixed amosite and wollastonite fibers. The estimate of the asbestos fraction, however, had a precision of 0.11 ( $s_r$ ). When this fraction was applied to the PCM count, the overall precision of the combined analysis was 0.20 [2].

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